

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11) Publication number:

**0 346 706 B1**

(12)

## EUROPEAN PATENT SPECIFICATION

(43) Date of publication of patent specification: **02.11.95** (51) Int. Cl.<sup>6</sup>: **C08K 5/34**, C08L 69/00

(21) Application number: **89110091.9**

(22) Date of filing: **03.06.89**

(54) **Polycarbonate compositions resistant to gamma radiation.**

(30) Priority: **16.06.88 US 207601**

(43) Date of publication of application:  
**20.12.89 Bulletin 89/51**

(45) Publication of the grant of the patent:  
**02.11.95 Bulletin 95/44**

(84) Designated Contracting States:  
**DE FR GB IT SE**

(56) References cited:  
**EP-A- 0 228 525**  
**US-A- 4 624 672**

(73) Proprietor: **Bayer Corporation**  
**One Mellon Center**  
**500 Grant Street**  
**Pittsburgh, PA 15219-2502 (US)**

(72) Inventor: **Lundy, Charles E.**  
**1014 Chestnut Ridge**  
**Pittsburgh, PA. 15205 (US)**  
Inventor: **Krishnan, Sivaram**  
**1653 Little Meadow Rd.**  
**Pittsburgh, PA. 15241 (US)**  
Inventor: **Reinert, Gerard E.**  
**304 Friar Lane**  
**McMurray, PA. 15317 (US)**

(74) Representative: **Gremm, Joachim, Dr. et al**  
**Bayer AG**  
**Konzernzentrale RP**  
**Patente Konzern**  
**D-51368 Leverkusen (DE)**

**EP 0 346 706 B1**

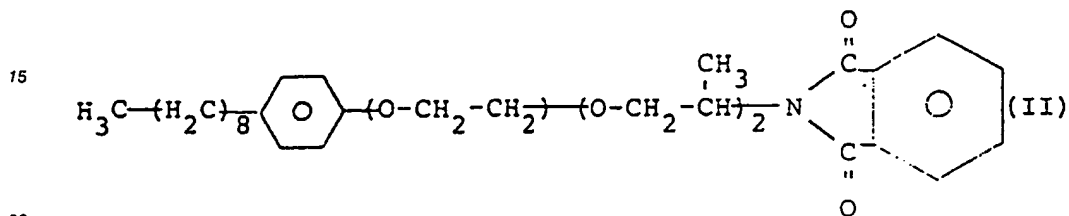
Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

**Description**Field of the Invention

5 The invention is directed to polycarbonate folding compositions and more particularly to thermoplastic compositions resistant to gamma radiation.

Summary of the Invention

10 The invention relates to thermoplastic polycarbonate molding compositions comprising a polycarbonate resin and a stabilizing agent conforming to formula (II)



The agent is homogeneously distributed throughout the resin and is present in an amount sufficient to improve the gamma radiation resistance of the composition.

25 BACKGROUND OF THE INVENTION

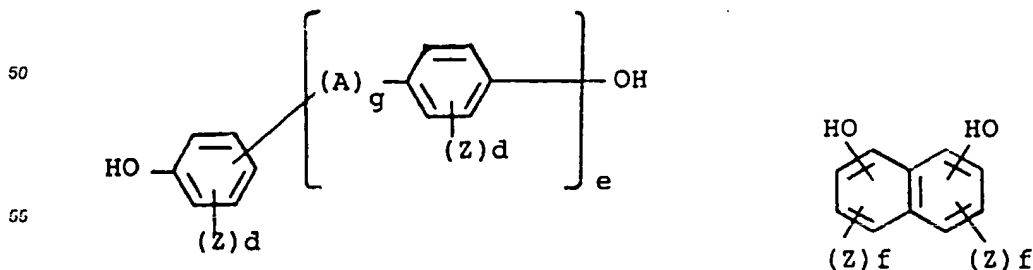
Because of its physical and mechanical properties polycarbonate resin was found to be eminently suitable for a variety of applications in the medical field. Applications which require sterilization by exposure to gamma radiation present a problem since polycarbonate tends to yellow and show increased haze. The art is noted to include US-A-4,624,972 which disclosed polycarbonate compositions resistant to gamma radiation containing an ester of an aromatic polycarboxylic acid. Polycarbonate compositions which are rendered gamma-ray resistant by the incorporation of polyether polyols are disclosed in EP-A-228,525.

DETAILED DESCRIPTION OF THE INVENTION

35 The composition of the invention comprises a polycarbonate resin and a stabilizing agent in an amount sufficient to enhance the resistance of the resin to yellowness and to the formation of haze upon exposure to gamma radiation. Preferably, the composition contains about 0.1 to 10.0 percent of the stabilizing agent.

40 The polycarbonate resins useful in the practice of the invention are homopolycarbonates, copolycarbonates and terpolycarbonates or mixtures thereof. The polycarbonates generally have a weight average molecular weight of 10,000-200,000, preferably 20,000-80,000 and their melt flow rate, per ASTM D-1238 at 300°C, is about 1 to about 65 gm/10 min., preferably about 2-15 gm/10 min. They may be prepared, for example, by the known diphasic interface process from a carbonic acid derivative such as phosgene and dihydroxy compounds by polycondensation.

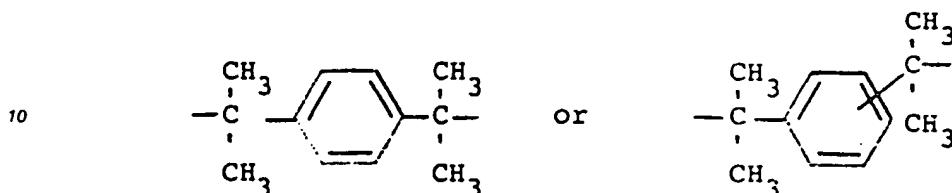
45 In the present context, dihydroxy compounds suitable for the preparation of the polycarbonates of the invention conform to the structural formulae (1) or (2)



wherein

A denotes an alkylene group with 1 to 8 carbon atoms, an alkylidene group with 2 to 8 carbon atoms, a cycloalkylene group with 5 to 15 carbon atoms, a cycloalkylidene group with 5 to 15 carbon atoms, a carbonyl group, an oxygen atom, a sulfur atom, -SO- or -SO<sub>2</sub>- or a radical conforming to

5



15 e and g both denote the number 0 to 1;

Z denotes F, Cl, Br or C<sub>1</sub>-C<sub>4</sub>-alkyl and if several Z radicals are substituents in one aryl radical, they may be identical or different one from the other;

d denotes an integer of from 0 to 4; and

f denotes an integer of from 0 to 3.

20 Among the dihydroxy compounds useful in the practice of the invention are hydroquinone, resorcinol, bis-(hydroxyphenyl) alkanes, bis-(hydroxyphenyl) ethers, bis-(hydroxyphenyl)-ketones, bis-(hydroxyphenyl)-sulfoxides, bis-(hydroxyphenyl)-sulfides, bis-(hydroxyphenyl)-sulfones, and  $\alpha,\alpha'$ -bis-(hydroxyphenyl)-diisopropyl-benzenes, as well as their nuclear-alkylated compounds. These and further suitable aromatic dihydroxy compounds are described, for example, in US-A-3,028,356; 2,999,835; 3,148,172; 2,991,273; 3,271,367; and 2,999,846. Further examples of suitable bisphenols are 2,2-bis-(4-hydroxyphenyl)-propane (bisphenol-A), 2,4-bis-(4-hydroxyphenyl)-2-methyl-butane, 1,1-bis-(4-hydroxyphenyl)-cyclohexane,  $\alpha,\alpha'$ -bis-(4-hydroxyphenyl)-p-diisopropylbenzene, 2,2-bis-(3-methyl-4-hydroxyphenyl)-propane, 2,2-bis-(3-chloro-4-hydroxyphenyl)-propane, bis-(3,5-dimethyl-4-hydroxyphenyl)methane, 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-propane, bis-(3,5-dimethyl-4-hydroxyphenyl)-sulfide, bis-(3,5-dimethyl-4-hydroxyphenyl)-sulfoxide, 30 bis-(3,5-dimethyl-4-hydroxyphenyl)-sulfone, hydroxybenzophenone, 2,4-bis-(3,5-dimethyl-4-hydroxyphenyl)-cyclohexane,  $\alpha,\alpha'$ -bis-(3,5-dimethyl-4-hydroxyphenyl)-p-diisopropylbenzene and 4,4'-sulfonyl diphenol.

Examples of particularly preferred aromatic bisphenols are 2,2-bis-(4-hydroxyphenyl)-propane, 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-propane and 1,1-bis-(4-hydroxyphenyl)-cyclohexane.

The most preferred bisphenol is 2,2-bis-(4-hydroxyphenyl)-propane (bisphenol-A).

35 The polycarbonates of the invention may entail in their structure units derived from one or more of the suitable bisphenols.

Among the resins suitable in the practice of the invention are included phenolphthalein-based polycarbonate, copolycarbonates and terpolycarbonates such as are described in US-A-3,036,036 and 4,210,741.

40 The polycarbonates of the invention may also be branched by condensing therein small quantities, e.g., 0.05-2.0 mol % (relative to the bisphenols) of polyhydroxyl compound. Polycarbonates of this type have been described. The following are some examples of polyhydroxyl compounds which may be used for this purpose: phloroglucinol; 4,6-dimethyl-2,4,6-tri-(4-hydroxyphenyl)-heptane; 1,3,5-tri-(4-hydroxyphenyl)-benzene; 1,1,1-tri-(4-hydroxyphenyl)-ethane; tri-(4-hydroxyphenyl)-phenylmethane; 2,2-bis-[4,4'-(4,4'-dihydroxydiphenyl)-cyclohexyl]-propane; 2,4-bis-(4-hydroxy-1-isopropylidene)-phenol; 2,6-bis-(2'-dihydroxy-5'-methylbenzyl)-4-methylphenol; 2,4-dihydroxy-benzoic acid; 2-(4-hydroxyphenyl)-2-(2,4-dihydroxyphenyl)-propane and 1,4-bis-(4,4'-dihydroxytriphenylmethyl)-benzene. Some of the other polyfunctional compounds are 2,4-dihydroxy-benzoic acid, trimesic acid, cyanuric chloride and 3,3-bis-(4-hydroxyphenyl)-2-oxo-2,3-dihydroindole.

50 In addition to the polycondensation process mentioned above, other processes for the preparation of the polycarbonates of the invention are polycondensation in a homogeneous phase and transesterification. The suitable processes are disclosed in the US-A-3,028,365; 2,999,846; 3,153,008; and 2,991,273.

The preferred process for the preparation of polycarbonates is the interfacial polycondensation process.

Other methods of synthesis in forming the polycarbonates of the invention such as disclosed in US-A-3,912,688, may be used.

55 Suitable polycarbonate resins are available in commerce, for instance, under the tradenames Makrolon® FCR, Makrolon® 2600, Makrolon® 2800 and Makrolon® 3100, all of which are bisphenol A based homopolycarbonate resins differing in terms of their respective molecular weights and characterized in that their melt flow indices (MFR) per ASTM D-1238 are about 16.5-24, 13-16, 7.5-13.0 and 3.5-6.5 gm/10 min.,

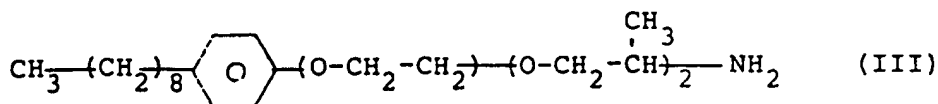
respectively. These are products of Mobay Corporation of Pittsburgh, Pennsylvania.

In the following examples which all parts and percentages are by weight unless otherwise specified.

### EXAMPLES

#### EXAMPLE 1 Preparation of a stabilizer - polyalkylene oxide phthalimide

A polyether conforming structurally to Formula II above was prepared by reacting 250 gm of Jeffamine-750 - a commercial product of Texaco conforming to



with 51 gm of phthalic anhydride in 400 ml of toluene, in a 1 liter-3 necked flask equipped with an agitator and a Dean stark trap with a condenser. The materials were charged into the flask and the temperature raised to 45°C. After reflux and azeotropic removal of water the reaction was allowed to cool.

#### EXAMPLE 2

Compositions of the invention containing the stabilizer which was prepared in accordance with Example 1 above were evaluated as to their optical properties (Yellowness Index = YI) both before and after exposure to gamma radiation. The Tables below summarize the results of the evaluation and include a comparison between compositions containing no stabilizer and composition containing 0.5% and 1% of the stabilizer. In the comparisons the polycarbonate resin was Makrolon® 2608 which is a bisphenol-A based homopolymer having a melt flow index of about 12-16 gm/10 min. The test specimens which were tested and reported in Table 1 were molded at 288°C and the one in Table 2 were molded at 343°C.

TABLE 1

Composition	YI (before radiation)	YI (after 5.0 Mrads)
Makrolon® 2608	3.95	13.07
Makrolon® 2608 with 0.5% polyalkylene oxide phthalimide	3.92	11.51
Makrolon® 2608 with 1.0% polyalkylene oxide phthalimide	4.25	9.25

TABLE 2

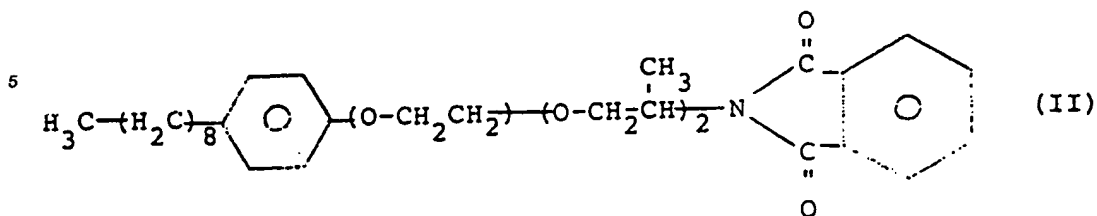
Composition	YI (before radiation)	YI (after 5.0 Mrads)
Makrolon® 2608	4.20	12.60
Makrolon® 2608 with 0.5% polyalkylene oxide phthalimide	4.30	10.67
Makrolon® 2608 with 1.0% polyalkylene oxide phthalimide	4.70	8.62

The compositions of the invention may be prepared by following conventional procedures for the preparation of thermoplastic polycarbonate molding compositions. The stabilizing agent may be introduced by directly mixing it with the polycarbonate. Other conventional additives may also be incorporated in the composition for their art-recognized utility. These include release agents, plasticizers, other stabilizers, antioxidants, fillers, reinforcements and the like.

### Claims

1. A polycarbonate molding composition comprising a homogeneous blend of
  - (i) an aromatic polycarbonate resin and

(ii) a stabilizing agent conforming to formula (II)

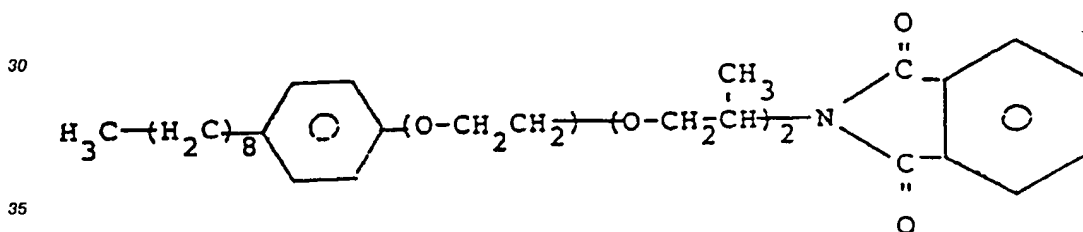


said (ii) being present in the composition in an amount sufficient to render the composition improved resistance to gamma radiation.

- 15
2. The composition of Claim 1 wherein said sufficient amount is 0.05 to 10 percent relative to the weight of the composition.
  3. The composition of Claim 1 wherein said polycarbonate is a homopolymer based on bisphenol A.
  - 20 4. Use of the composition of Claim 1 for injection moulding polycarbonate articles.

#### Patentansprüche

- 25
1. Polycarbonat-Formmasse, umfassend ein homogenes Gemisch von
    - (i) einem aromatischen Polycarbonatharz und
    - (ii) einem Stabilisator, der der Formel (II) entspricht



wobei (ii) in der Masse in einer ausreichenden Menge vorliegt, um der Masse eine verbesserte Beständigkeit gegenüber Gammastrahlung zu verleihen.

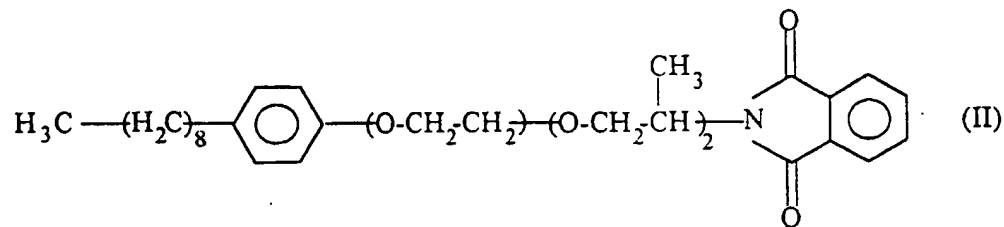
- 40
2. Masse gemäß Anspruch 1, wobei die ausreichende Menge 0,05 bis 10 Prozent beträgt, bezogen auf das Gewicht der Masse.
  3. Masse gemäß Anspruch 1, wobei das Polycarbonat ein Homopolymer auf der Basis von Bisphenol A ist.
  - 45 4. Verwendung der Masse gemäß Anspruch 1 zum Spritzgießen von Polycarbonatgegenständen.

#### Revendications

- 50
1. Composition de polycarbonate pour moulage constituée par un mélange homogène de
    - (i) une résine polycarbonate aromatique et

55

(ii) un agent stabilisant ayant la formule (II)



15 ledit (ii) étant présent dans la composition en une quantité suffisante pour conférer à la composition une plus grande résistance aux rayonnements gamma.

- 20
2. Composition selon la revendication 1, dans laquelle ladite quantité suffisante est comprise entre 0,05 et 10 % par rapport à la masse de la composition.
  3. Composition selon la revendication 1, dans laquelle ledit polycarbonate est un homopolymère à base de bisphénol A.
  4. Utilisation de la composition selon la revendication 1, pour réaliser des articles en polycarbonate moulés par injection.
- 25
- 30
- 35
- 40
- 45
- 50
- 55